

<特開2000-154049>

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Patent Assignee; NIPPON SHOKUBAI CO., LTD.

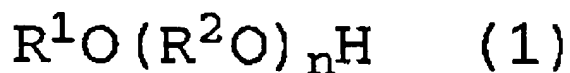
Title of the Invention: STORAGE AND TRANSFER METHOD OF
ALKOXPOLYALKYLENE GLYCOL

[Claims]

[Claim 1] A storage and transfer method of an alkoxy polyalkylene glycol to be used as a raw material for a cement dispersant, wherein alkoxy polyalkylene glycol defined by the formula

(1):

[formula 1]



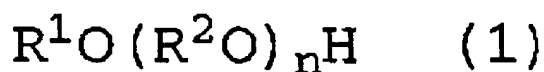
in the formula, R^1 represents a hydrocarbon group containing 1 to 30 carbon atoms, R^2O group represents an oxyalkylene group containing 2 to 18 carbon atoms, each R^2O group may be the same or different and the respective repeating units of R^2O group may form block adducts or random adducts in the case R^2O group is in form of a mixture of two or more kinds of the repeating units, and n represents the average number of moles of oxyalkylene groups and is a number of 1 to 300, is stored and transferred in a vessel in the atmosphere produced by purging the air with an inert gas and/or adding a radical capturing agent in the vessel.

[Claim 2] The method according to claim 1, wherein the alkoxy polyalkylene glycol is stored and transferred in the atmosphere produced by purging not less than 70% of the total capacity of the air in the vessel with an inert gas.

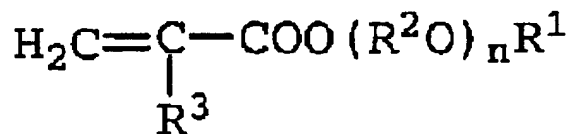
[Claim 3] The method according to claim 1, wherein the radical capturing agent is tert-butylhydroxytoluene.

[Claim 4] The method according to claim 1 or 3, wherein the addition amount of the radical capturing agent is 10 to 1,500 ppm relative to the amount of alkoxy polyalkylene glycol.

[Claim 5] A production method of a polymer to be used for a cement dispersant by carrying out esterification of an alkoxy polyalkylene glycol represented by the formula (1):
[formula 1]



in the formula, R^1 represents a hydrocarbon group containing 1 to 30 carbon atoms, R^2O group represents an oxyalkylene group containing 2 to 18 carbon atoms, each R^2O group may be the same or different and in the case R^2O group is in form of a mixture of two or more kinds of the repeating units, the respective repeating units of R^2O group may form block adducts or random adducts, and n represents the average number of moles of oxyalkylene groups and is a number of 1 to 300, with (meth)acrylic acid for obtaining alkoxy polyalkylene glycol mono(meth)acrylic acid ester represents by the formula (3):
[formula 3]



in the formula, R^1 , R^2 , and n are same as described above, and R^3 is hydrogen atom or methyl group, and polymerizing the alkoxy polyalkylene glycol mono(meth)acrylic acid ester with (meth)acrylic acid (salt) and, if necessary, a monomer copolymerizable with the alkoxy polyalkylene glycol mono(meth)acrylic acid ester or (meth)acrylic acid (salt), wherein the alkoxy polyalkylene glycol is as claimed in one of claims 1 to 4.

[Claim 6] A cement dispersant comprising at least the polymer

produced by the method according to claim 5.

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[0066] (II) Partial neutralization step

This step is carried out in order to solve the following problems and the step involves neutralization of the acid catalyst at 90°C or lower with an alkali after completion of the esterification according to the above-mentioned esterification step (1). The problems are: in the case when azeotropic treatment is carried out by adding water in the step of removing the dehydrated solvent by distillation after the esterification or in the case when an aqueous solution of the esterified product is prepared by adding adjustment water after esterification for further polymerization of the esterified product, hydrolysis is occurred by an acid catalyst, as the results, leading to the deterioration of the quality and the performance of the esterified product and the remaining of residues produced by the hydrolysis (hereinafter, simply referred to as hydrolyzed products) in the esterified product. In the case when a polymer to be used as a cement dispersant is produced by using the esterified product, the hydrolyzed products become impurities irrelevant to the polymerization, the polymerization ratio (consequently productivity) is decreased, thereby the quality and the performance of the polymer are deteriorated.

[0113] Example 4

A reaction vessel (3L in inner capacity) made of glass and equipped with a thermometer, a stirrer, a produced water separator, and a refluxing condenser were filled with 1,346 g of alkoxypolyalkylene glycol (2) obtained in Example 2, 654 g of methacrylic acid, and 660 g of benzene as a dehydrated solvent,

20 g of sulfuric acid as an acid catalyst, and 0.5 g of hydroquinone as a polymerization inhibitor, and while the mixed solution being stirred, the temperature was increased to 90°C and esterification was started. After it was confirmed that the 52 ml of produced water was removed, 118 g of an aqueous solution of 30% sodium hydroxide and 370 g of water were added to remove benzene by azeotropic treatment with water, then adjustment water was added to obtain an aqueous solution of 80% monomer mixture (1). No gel was formed during the above-mentioned esterification.

[0114]

Then, a reaction vessel (3L in inner capacity) made of glass and equipped with a thermometer, a stirrer, a dropping funnel, a nitrogen gas inlet tube and reflux condenser was filled with 1,900 g of water. Under stirring condition, the inside of the reaction vessel was purged with nitrogen and in the nitrogen atmosphere, water was heated to 95°C. Further, a mixed solution of the aqueous solution obtained by adding 1,000 g of water to 1,000 g of 80% monomer mixture (1) obtained in the above-mentioned manner was added dropwise to the reaction vessel over 4 hours and then an aqueous solution obtained by dissolving 13.5 g of ammonium persulfate in 86.5 g of water was added dropwise over 5 hours. After completion of the dropwise addition, the reaction temperature was further maintained at 95°C for 1 hour to complete the polymerization and the resulting reaction solution was neutralized to pH 7 with a 30% aqueous solution of sodium hydroxide to obtain an aqueous polymer solution (1) of the present invention having a weight average molecular weight (on the basis of polyethylene glycol by gel permeation chromatography (GPC); hereinafter the same) of 33,000.

[0115] Example 5

Esterification is carried out in the same manner as that of Example 4 to obtain an aqueous solution of 80% monomer mixture (2), except that alkoxypolyalkylene glycol (3) obtained in Example 2 was used instead of using the alkoxypolyalkylene glycol (2). No gel was formed during the esterification.

[0116]

Then, an aqueous polymer solution (2) of the present invention with a weight average molecular weight of 33,000 was obtained by completing polymerization and carrying out the neutralization in the same manner as that of Example 4, except that the aqueous solution of 80% monomer mixture (2) was used.

[0117] Comparative Example 2

When esterification was started in the same manner as that of Example 4 except that the alkoxypolyalkylene glycol (4) obtained in Comparative Example 1 was used instead of using the alkoxypolyalkylene glycol (2), a large amount of gel adhered to the stirring blades, stirring shaft and the thermometer and therefore, the esterification was stopped. The resulting reaction mixture was filtered to remove the gel and separate methoxypoly(n = 10)ethylene glycol monomethacrylate.

[0118]

Then, an aqueous polymer solution (1) for comparison with a weight average molecular weight of 33,000 was obtained by completing polymerization and carrying out the neutralization in the same manner as that of Example 4, except that a mixture obtained by adding 265 g of methacrylic acid to 1,000 g of thus obtained methoxypoly(n = 10)ethylene glycol monomethacrylate was used instead of using the aqueous solution of 80% monomer mixture (1) in Example 4.

[0119]

The results obtained in Examples 4, 5 and Comparative Example 2 are summarized in the following Table 2.

[0120]

Table 2

	Alkoxypolyethylene glycol used	Formation of gel during esterification	Weight average molecular weight of the obtained polymer
Example 4	Alkoxypolyalkylene glycol (2)	none	33,000
Example 5	Alkoxypolyalkylene glycol (3)	none	33,000
Comparative Example 2	Alkoxypolyalkylene glycol (4)	A large amount of gel produced	33,000*

*: polymerization after removal of gel by filtration

[0121]

From the results in Table 2, it was found that in the case when the alkoxypolyalkylene glycol (2) stored for 1 week under nitrogen atmosphere or the alkoxypolyalkylene glycol (3) stored for 1 week under atmosphere in which BHT was added was used for esterification, gel was not produced at all, while in the case when the alkoxypolyalkylene glycol (4) stored for 1 week in air was used for esterification, a large amount of gel was produced. Also, it was found that the aqueous solutions of monomer mixtures obtained by esterification using the alkoxypolyalkylene glycol (2) or the alkoxypolyalkylene glycol (3) could be used for polymerization without any previous treatment, while in the case of using the aqueous solution of the monomer mixture obtained by esterification of the alkoxypolyalkylene glycol (4), an extra step for removing gel produced was required before the polymerization was carried out.